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Improved efficiency of NiO_x-based p-i-n perovskite solar cells by using PTEG-1 as electron transport layer

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We present efficient p-i-n type perovskite solar cells using NiO_x as the hole transport layer and a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain (PTEG-1) as electron transport layer. This electron transport layer leads to higher power conversion efficiencies compared to perovskite solar cells with PCBM (phenyl-C₆₁-butyric acid methyl ester). The improved performance of PTEG-1 devices is attributed to the reduced trap-assisted recombination and improved charge extraction in these solar cells, as determined by light intensity dependence and photoluminescence measurements. Through optimization of the hole and electron transport layers, the power conversion efficiency of the NiO_x/perovskite/PTEG-1 solar cells was increased up to 16.1%. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4992783>]

Hybrid inorganic-organic perovskite solar cells have attracted considerable attention because of their high power conversion efficiencies, owing to their strong absorption over a wide range of the solar spectrum, long electron-hole diffusion lengths, and ambipolar charge transport characteristics.^{1–6} These solar cells have been reported both in the n-i-p and in the p-i-n structure. However, n-i-p type planar cells, where the perovskite layer is sandwiched between TiO₂ and the hole transport layer, suffer from severe hysteresis, as opposed to p-i-n cells.^{7–9} A commonly used hole transport layer (HTL) in p-i-n solar cells is poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). However, perovskite solar cells with this HTL typically have a lower open-circuit voltage (V_{OC}) than the cells based on TiO₂.⁸ In addition, solar cells incorporating PEDOT:PSS are sensitive to degradation, which is detrimental for long-term operation.¹⁰

Inorganic materials, such as metal oxides, are more stable alternatives as HTLs because they are less prone to degradation under a variety of conditions.^{11–13} NiO_x is an example of an inorganic HTL with good chemical stability and suitable work function (−4.8 eV) for p-i-n perovskite solar cells.^{14,15} The V_{OC} of NiO_x-based perovskite solar cells is typically higher than that of PEDOT:PSS devices (1 V and 0.9 V, respectively), leading to higher power conversion efficiencies.^{15,16}

PCBM (phenyl-C₆₁-butyric acid methyl ester) is commonly used as the electron transport layer in the p-i-n structure, but this material is often combined with other layers, such as bathocuproine (BCP), to block holes and improve the power conversion efficiency.^{15,17,18} Incorporating additional layers into the solar cell's device structure leads to increased complexity in processing, and therefore it is desirable to replace the electron transport layer to simplify the overall device structure. Recently, Yin *et al.* showed NiO_x-based solar cells with only PCBM as the electron transport layer (ETL), reaching a power conversion efficiency (PCE) of 15.7%.¹⁹ However, their solar cells have a V_{OC} lower

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than 1 V, which limits their efficiency. Our previous work on PEDOT:PSS-based p-i-n perovskite solar cells demonstrated that the PCE increases when PCBM is replaced by PTEG-1, which is a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain.^{9,20}

In this paper, we report the first use of PTEG-1 in perovskite solar cells with a NiO_x hole transport layer. We compare the performance of solar cells with PTEG-1 to PCBM-based devices and conclude that the use of PTEG-1 can lead to higher PCEs up to 16.1% with open-circuit voltages as high as 1.12 V.

The device structure used in this work is ITO/NiO_x/CH₃NH₃PbI₃/ETL/Al, as shown in Fig. 1(a). The chemical structures of the two materials used as ETLs, PCBM, and PTEG-1, are displayed in Fig. 1(b). The high quality and low roughness of the NiO_x layer (Fig. S1 of the [supplementary material](#) shows the atomic force microscopy (AFM) image of a NiO_x film) enables a good coverage of the perovskite film.

The perovskite layer is deposited from a mixture of high boiling point solvents, based on the method reported by Jeon *et al.*⁶ Figure S2 of the [supplementary material](#) displays the scanning electron microscopy (SEM) images of a uniform and pinhole-free perovskite film deposited on a NiO_x film. From these images it is clear that the perovskite grains are extremely large (on the order of tens to hundreds of microns) and that the surface is completely covered.

Figure 2(a) shows the current density–voltage (*J*–*V*) characteristics of the solar cells with PTEG-1 and PCBM as electron transport layers under AM1.5G illumination. The *J*–*V* parameters are summarized in Table I. The solar cell with PCBM reaches 11.8% power conversion efficiency, with a short-circuit current density (*J*_{SC}) of 19.6 mA/cm², an open-circuit voltage of 1.09 V and a fill factor (FF) of 55%. When PTEG-1 is used instead of PCBM, the *V*_{OC} and *J*_{SC} increase to 1.11 V and 21.4 mA/cm², respectively. This results in a higher PCE of 13.1%, since the fill factor does not change.

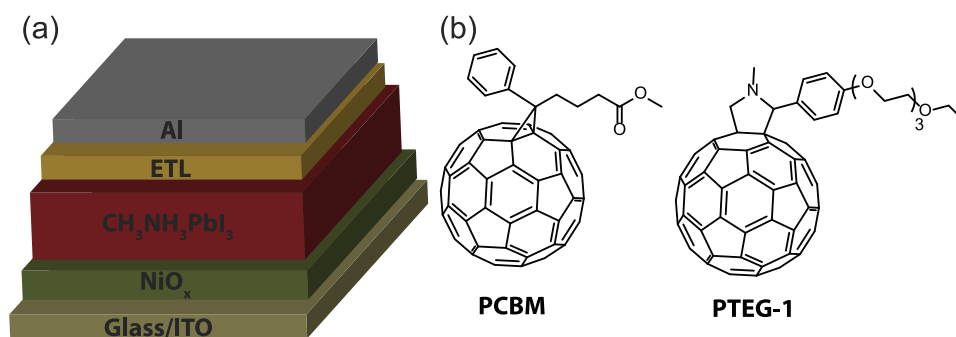


FIG. 1. (a) Schematic device structure of a perovskite solar cell; the stacking is: ITO/NiO_x/CH₃NH₃PbI₃/ETL/Al. (b) Chemical structures of PCBM and PTEG-1, which are used as ETLs.

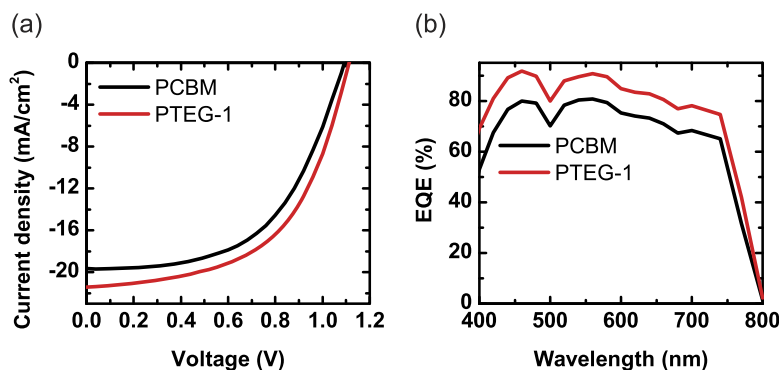


FIG. 2. (a) *J*–*V* curve for different ETLs in the glass/ITO/NiO_x/CH₃NH₃PbI₃/ETL/Al device structure. (b) EQE spectra of the devices in (a). The layer thicknesses of NiO_x, perovskite, PCBM and PTEG-1 are 40 nm, 270 nm, 65 nm and 60 nm, respectively.

TABLE I. Device performances for different ETLs.

ETL	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
PCBM	19.6	1.09	55	11.8
PTEG-1	21.4	1.11	55	13.1

Our group has previously reported improvements in V_{OC} and J_{SC} after replacing PCBM by PTEG-1 in hybrid perovskite devices using PEDOT:PSS as the hole extraction layer. This improvement was attributed to the reduction of trap-assisted recombination in the case of PTEG-1.⁹ We carried out light intensity dependence measurements to determine the reason for the increased performance in the current device structure and the results are displayed in Fig. S3 of the [supplementary material](#). The dependence of V_{OC} on the light intensity should be linear when plotted in a semi-logarithmic scale, which is the case in Fig. S3. We can extract the diode ideality factor n (in units of kT/q , where k is Boltzmann's constant, T is the absolute temperature, and q is the elementary charge) from the slope of the fit. When n is equal to 1, only bimolecular recombination takes place in the device. Trap-assisted recombination is characterized by n between 1 and 2.²¹ In our case, the values of n for PCBM and PTEG-1 are 1.37 and 1.21, respectively. This indicates that the trap-assisted recombination is lower in the case of PTEG-1. Figure 2(b) shows the external quantum efficiency (EQE) spectra of the ITO/NiO_x/perovskite/ETL/Al devices for both PCBM and PTEG-1. The EQE of the PTEG-1 device is higher than 80% over almost the entire wavelength range from 420 to 660 nm, and it is higher than that of PCBM over the full range of the measurement. The J_{SC} obtained by integration of the EQE spectra is in agreement with the J_{SC} obtained from the J - V measurements for both ETL layers (see Fig. S4 of the [supplementary material](#)).

To fully understand why our PTEG-1 solar cells perform better than the PCBM-based devices, we conducted photoluminescence (PL) measurements (see Fig. 3). With these measurements it is possible to study the charge carrier recombination upon excitation. The steady state PL was measured for stacks composed of glass/NiO_x/CH₃NH₃PbI₃/PCBM and glass/NiO_x/CH₃NH₃PbI₃/PTEG-1; the structure glass/NiO_x/CH₃NH₃PbI₃ was used as comparison. From the measurements in Fig. 3(a), it is clear that there is successful charge transfer from the perovskite layer to the ETLs, as indicated by the quenched PL signal. The quenching in the PTEG-1 sample is stronger than in the PCBM sample, which is supported by the time-resolved PL data shown in Fig. 3(b). This plot shows that the PL signal decays mono-exponentially for all samples. The lifetime of the PL signal is shorter for PTEG-1 ($\tau = 10.3$ ns) than for PCBM ($\tau = 25$ ns) and for the perovskite only ($\tau = 190$ ns). These results indicate that the charge extraction is better in the case of NiO_x/perovskite/PTEG-1 than in the case where PCBM is the ETL.

In order to improve the power conversion efficiency of the PTEG-1 solar cells, we attempted to optimize the thicknesses of the transport layers. Solar cells with different thicknesses of the PTEG-1

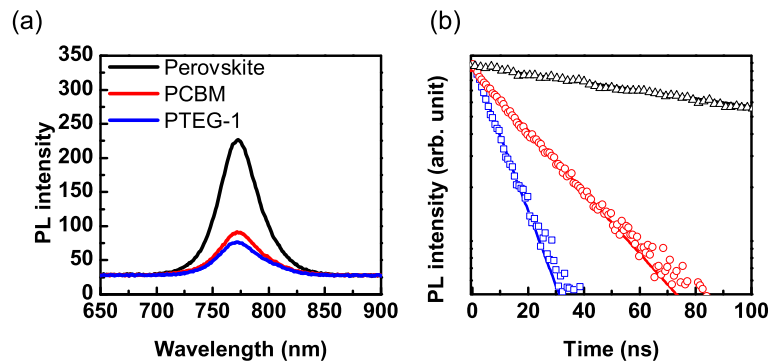


FIG. 3. (a) Steady state PL spectra for glass/NiO_x/CH₃NH₃PbI₃ (black line), glass/NiO_x/CH₃NH₃PbI₃/PCBM (red line) and glass/NiO_x/CH₃NH₃PbI₃/PTEG-1 (blue line). (b) Time-resolved PL of the samples in (a). Symbols show the data, the solid lines are the mono-exponential fits.

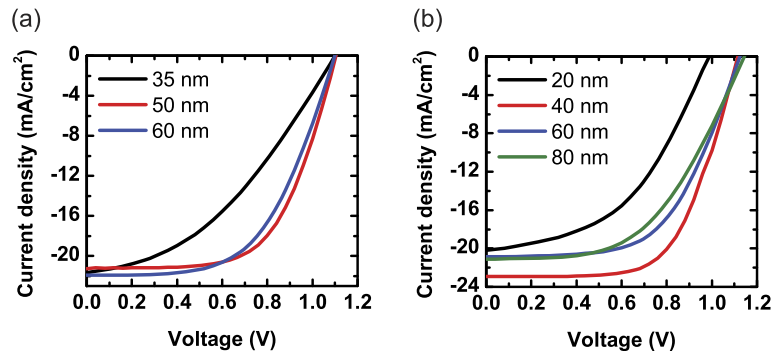


FIG. 4. (a) J - V curves of glass/ITO/NiO_x/CH₃NH₃PbI₃/PTEG-1/Al devices with different thicknesses of the PTEG-1 layer. (b) J - V measurements showing the influence of the thickness of NiO_x on the device performance. The perovskite and PTEG-1 thicknesses in these devices are 270 and 50 nm, respectively.

layer were made and the corresponding J - V measurements are presented in Fig. 4(a) and in Table II. It was found that when the PTEG-1 layer is thin (about 35 nm), the devices show current leakage. As a result the fill factor is low, which could be due to insufficient coverage of PTEG-1 on the perovskite surface. Increasing the PTEG-1 thickness improves the FF and PCE considerably. The device with 50 nm PTEG-1 has a fill factor of 61%, but increasing the thickness further (60 nm) lowers the FF to 56%. Therefore, 50 nm is the optimal thickness for this ETL. Below this thickness, there is the possibility of shunt pathways. However, above 50 nm there will be additional series resistance in the layer, which reduces the PCE.

Figure 4(b) shows the effect of the NiO_x thickness on the device performance; a slight change in the thickness has a large influence on the device performance. The thickness of the perovskite layer was 270 nm, the same as used in the cells from Fig. 4(a), and the PTEG-1 layers were 50 nm thick. The current density—voltage parameters are listed in Table III. It is evident that thicker layers lead to an increase in V_{OC} (from 0.99 to 1.14 V). The short-circuit current density and fill factor for the device with 20 nm NiO_x are 20.2 mA/cm² and 47%, respectively. When the thickness of the NiO_x layer is increased to 40 nm, both J_{SC} and FF increase. However, increasing the thickness beyond 40 nm does not lead to an overall better device performance, which is mainly caused by a reduction in the fill factor. This trend can be explained by the increased series resistance in the HTL. We can conclude here that the optimal thickness for NiO_x is 40 nm, and this gives a solar cell with a J_{SC} of 22.9 mA/cm², a V_{OC} of 1.12 V, a FF of 63% and a resulting PCE of 16.1%. This is among the highest reported values for a NiO_x/perovskite/fullerene solar cell. The value of 16.1% is the maximum value

TABLE II. Device performances for different thicknesses of PTEG-1 based on the structure glass/ITO/NiO_x(30 nm)/CH₃NH₃PbI₃(270 nm)/PTEG-1/Al.

PTEG-1 thickness (nm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
35	21.7	1.10	39	9.4
50	21.3	1.11	61	14.4
60	21.9	1.10	56	13.6

TABLE III. Device performances for different thicknesses of NiO_x for a device structure of glass/ITO/NiO_x/CH₃NH₃PbI₃(270 nm)/PTEG-1(50 nm)/Al.

NiO _x thickness (nm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
20	20.2	0.99	47	9.4
40	22.9	1.12	63	16.1
60	20.9	1.13	58	13.6
80	21.1	1.14	52	12.5

that we achieved; see Figs. S5 and S6 of the [supplementary material](#) for an overview of the power conversion efficiencies for devices prepared in the same way and the hysteresis in the champion device, respectively.

In summary, we have demonstrated that the power conversion efficiency of NiO_x -based p-i-n planar perovskite solar cells can be improved by changing the electron transport layer from PCBM to PTEG-1. This is mainly caused by the increased short-circuit current density when PTEG-1 is used. External quantum efficiency and photoluminescence measurements indicate that the charge extraction is more efficient for devices with PTEG-1 as ETL. In addition, we found that the solar cells with PTEG-1 suffer less from trap-assisted recombination compared to the PCBM counterparts. Optimization of the thicknesses of both the electron and hole transport layer lead to power conversion efficiencies up to 16.1% for $\text{ITO}/\text{NiO}_x/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PTEG-1}/\text{Al}$.

See [supplementary material](#) for details on device fabrication and characterization.

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